

CATALYSIS OF MULTI-COMPONENT LEWIS ACIDS FOR COAL HYDROLIQUEFACTION AND MODEL REACTIONS

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INTRODUCTION

Development of new catalysts is a promising approach to more efficient coal liquefaction. It has been recognized that dispersed catalysts are superior to supported catalysts for primary liquefaction, because the control of coal depolymerization or dissolution requires intimate contact between the catalyst and coal. The dispersed catalysts can be divided into metals and their oxides and sulfides (e.g. MoS₂), and acid catalysts such as ZnCl₂. An excellent review of coal liquefaction catalysts has been published recently by Derbyshire (1), which also incorporated many previous works on the catalytic effects of Lewis acids. In particular, the process development research conducted by Zielke and co-workers (2-4) at the Consolidation Coal Co. demonstrated the potential of using massive ZnCl₂ catalyst to liquify coals. The fundamental studies on model reactions by Bell and co-workers (5-8) at the University of California contributed to a mechanistic understanding of the catalytic effects of ZnCl₂ for coal liquefaction.

While ZnCl₂ and SnCl₂ have always been considered attractive because of their high activity and low cost, a considerable body of research at Osaka university has demonstrated that ZnCl₂ and SnCl₂ doped with alkali metal chlorides or transition metal chlorides are more effective for liquefaction of many bituminous, subbituminous and brown coals (9-13). One of the important observations from these works is that the addition of alkali metal chlorides to ZnCl₂ increases the yields of oils (hexane solubles) and decreases the gas yields and reduces H₂ consumption. This is desirable because hydrogen consumption is a major cost of coal liquefaction plant. With an attempt to develop new catalysts, we examined the catalytic effects of MCl_n-LiCl-NaCl-KCl and MCl_n-LiCl-KCl (MCl_n = CoCl₂, NiCl₂, MoCl₃, SnCl₂, ZnCl₂) for coal liquefaction. The results showed that NiCl₂- and MoCl₃-LiCl-KCl ternary salts are promising catalysts in view of high oil yields and coal conversions and lower heteroatom contents of oils (14-17), and they appeared to be superior to ZnCl₂-, SnCl₂- and CoCl₂-containing and other NiCl₂- and MoCl₃-containing salts (14,18). Little is known about the reaction chemistry, more specifically, the hydrogenation and cracking of polyaromatics and the cleavage of bridge structures during coal liquefaction using the NiCl₂- and MoCl₃-based catalysts. The purpose of this paper is to evaluate the catalysis of these two new catalysts based on coal liquefaction, pyrolysis, and model compound studies.

EXPERIMENTAL

The salts used are synthesized MoCl₃ (14), reagent grade NiCl₂, LiCl and KCl. The molar compositions of NiCl₂- and MoCl₃-LiCl-KCl and LiCl-KCl were 14:50:36, 12:51:37 and 58:42, respectively, unless otherwise mentioned. The catalysts were impregnated on to coals from their methanol solution or suspension. The coals used are Morwell (C: 67%, daf basis) brown, Taiheiyō (C: 76%), Wandoan (C: 78%) and Yilan (C: 79%) subbituminous, and Akabira (C: 83%) bituminous coals (14-17). The temperature-programmed pyrolysis was conducted by using TGA in a nitrogen flow (14,19). The solvent-free coal liquefaction was carried out in a 200 ml shaking autoclave at 400°C for 1 hour with 9.8 MPa H₂ (14-15). The liquefaction in the presence of tetralin was conducted in 70 ml rocking autoclaves at 400°C for 1 h with 4.9 MPa H₂ (17). The products were separated into gases, oils (hexane solubles), asphaltene (hexane-insoluble benzene solubles), preasphaltene (benzene-insoluble pyridine or THF solubles), and residue (16). The gases were analyzed by GC for C₁-C₄, CO and CO₂; the oils and asphaltene were subjected to ¹H NMR (15,17) and elemental analyses. The model compounds tested are anthracene, phenanthrene, naphthalene, dibenzyl, benzylphenylether, and dibenzylether. Their reactions were performed in the 70 ml autoclaves under different conditions. The products were analyzed by GC, and GC-MS (20).

RESULTS

Temperature-Programmed Pyrolysis. The non-catalytic pyrolysis of the five coals in N₂ was conducted using two temperature programs: r.t. to 600°C at 5°C/min; and r.t. to 400°C at 5°C/min and then held at 400°C for 60 min. The second program was also used in catalytic pyrolysis in accordance with the temperature/time conditions in liquefaction (14). Figure 1 shows the pyrolysis results of the five coals up to 600°C. The yields of volatile products were calculated from the weight loss determined by TGA. The weight loss below 200°C is mainly due to adsorbed water and was not accounted as volatile materials. The amounts of volatile materials formed below 450°C decreased with increasing rank, *daf* C% of the coals. Figure 2 presents the results of catalytic pyrolysis of Akabira coal in N₂. Figure 3 shows the temperature-pressure profiles during heat-up and holding at 400°C for solvent-free liquefaction of Akabira coal with 9.8 MPa H₂. The NiCl₂- and MoCl₃-LiCl-KCl catalysts began to exert a measurable effect in enhancing coal pyrolysis in N₂ at the temperatures above 300°C (Figure 2). During the heat-up of the coal impregnated with these catalysts under pressurized H₂, the H₂ uptake became apparent at the same temperature region, indicating the onset of the catalytic reactions at the temperatures as low as about 300°C (Figure 3). The same trends were observed in the pyrolysis (14, 19) and *t-p* profiles in liquefaction of other coals. The *t-p* profiles for liquefaction of Akabira coal in the presence of tetralin were similar to those for the solvent-free runs, except that the evaporation of tetralin caused the pressure increase (below 300°C).

Solvent-free Liquefaction. In general, acids are used in massive amounts (1-9) as catalysts and reaction medium. In this work, the concentration of Lewis acids in ternary salts for liquefaction were below 15 mol%. Figure 4 shows the results of solvent-free liquefaction of Australian Wandoan subbituminous coal (400°C, 1 h, 9.8 MPa H₂) using various MCl_n-LiCl-NaCl-KCl and MCl_n-LiCl-KCl (MCl_n: 12-14 mol%, salts to coal: 1, wt ratio), where the yields of products are plotted against H₂ consumptions. It is clear from the product distribution that NiCl₂- and MoCl₃-LiCl-KCl afforded over 60% (*daf* coal basis) oils and showed higher selectivity to oils without remarkable increase in gas-make. The previous results for Wandoan coal (3 h runs, other conditions were the same) using ZnCl₂ and ZnCl₂-KCl (60:40, mol%) are also shown in Figure 4. Relative to ZnCl₂, ZnCl₂-KCl gave higher oil yield and lower gas yield with lower H₂ consumption, as has been observed for many other coals (9-11). Although the catalysts and reaction time were different, the results in Figure 4 showed that higher oil yields can be obtained with relatively lower H₂ consumption.

In order to examine the general effectiveness of the new catalysts, we conducted the solvent-free liquefaction of Australian Morwell coal, Japanese Taiheiyō and Akabira coals under the same conditions (400°C, 1 h, 9.8 MPa H₂). The results are summarized in Figure 5. Relative to the thermal runs, both NiCl₂- and MoCl₃-LiCl-KCl catalysts significantly enhanced coal conversion. More importantly, the oil yields of all the catalytic runs are almost three times that of non-catalytic runs of the bituminous, subbituminous and brown coals. These results established the general applicability of these two catalysts for liquefaction of coals, especially subbituminous coals (oil yields: ≥ 56%). ¹H NMR and elemental analyses revealed that the catalysts increased the contents of naphthenic CH₂ hydrogens (hydroaromatics) and decreased the O and N contents of oils.

Liquefaction in the Presence of H-Donor. In a previous work, addition of tetralin was found to further increase the conversion of coal, although this effect was substantially smaller in the catalytic runs than in the non-catalytic run (16). The NiCl₂- and MoCl₃-based catalysts played a key role in promoting oil production, while adding tetralin appeared to enhance the selectivity of the catalytic reactions, in view of increased conversion and decreased total hydrogen consumption. Based on these observations, we examined the catalyst performance at different loading levels for liquefaction of Chinese Yilan coal in the presence of tetralin under low H₂ pressure (400°C, 1 h, 4.9 MPa H₂; tetralin/coal: 5g/5g; metal to coal: Ni, 1.2-12 wt%; Mo, 1.7-17 wt%). Figures 6 and 7 show the effect of catalyst loading on the product distribution and hydrogen transfer, respectively. The loading of NiCl₂-LiCl-KCl to coal up to 20wt% (2.4wt% Ni to coal) significantly increased oil yields, coal conversions, enhanced gas-phase H₂ consumptions but decreased the net hydrogen-transfer from tetralin (Figure 6B). Further increase in its loading resulted in a little decrease in gas-phase H₂ and total hydrogen consumptions, in spite of the increase in oil yield. In the case of MoCl₃-LiCl-KCl, increase in its loading progressively increased oil yields and gas-phase H₂ consumptions and decreased the net hydrogen-transfer from tetralin (Figure 6A). In contrast to these trends, the use of LiCl-KCl, even at low loading, considerably suppressed the gas-phase H₂ consumption without any negative impact on the product distribution (Figure 6C).

Figure 7 shows the effect of catalyst loading on H-distribution of oils per 100 C atoms, as determined from NMR (17). The HCH_3 values indicate the contents of alpha-, beta- and gamma- CH_3 hydrogens and gamma- CH_2 hydrogens; the HCH_2 refers to the alpha- and beta- CH_2 hydrogens. As shown in Figure 7, the HCH_2 values increased, but HCH_3 decreased with catalyst loading, reflecting that loading the catalysts increased the contents of naphthenic CH_2 hydrogens present in hydroaromatic rings. These trends were also observed in the ^1H NMR analysis of oils from solvent-free liquefaction of the other four coals (15-16).

Model Compounds Studies. To gain a better understanding of the catalytic functions, the model reactions were undertaken using NiCl_2 , MoCl_3 , LiCl-KCl , and their combinations. Tables 1 and 2 present the results for anthracene and phenanthrene (400°C , 1 h, 9.8 MPa H_2), respectively, with constant molar ratio (0.3) of NiCl_2 or MoCl_3 to the reactant (3 g, 16.85 mmol). As shown in Table 1, both NiCl_2 - and MoCl_3 - LiCl-KCl considerably promoted the hydrogenation of anthracene to form tetra- and octahydroanthracene. In the runs of phenanthrene, which is known to have lower reactivity (20), the catalysts enhanced the formation of di- and tetrahydrophenanthrene. In the runs of naphthalene, these catalysts promoted hydrogenation to produce tetralin, but the conversions were within 15%. As shown in Tables 1-2, the use of LiCl-KCl gave nearly identical results to the thermal runs. However, adding LiCl-KCl to NiCl_2 and MoCl_3 , especially to MoCl_3 which exhibited very high cracking activity, significantly suppressed the extensive hydrogenation and ring-opening cracking. Figure 8 shows the effect of MCl_n content in the runs of anthracene. The yields of hydroaromatics and cracking products appeared to depend on the contents of Lewis acids MCl_n , especially in the case of MoCl_3 .

Table 3 is a summary of the bond dissociation energy of a number of C-O and C-C linkages. Various connecting linkages between aromatic rings are believed to be present in coals. We conducted model reactions of C-O linkage structures using benzylphenylether and dibenzylether at 350°C for 1 h with 4.9 MPa H_2 . As shown in Table 4, the presence of the salts significantly affected the reactions of the ethers. The use of NiCl_2 - and MoCl_3 - LiCl-KCl decreased the yields of simple products such as toluene, and increased the yields of the products from rearrangement and coupling reactions such as PhCH_2PhOH and $\text{PhCH}_2(\text{PhCH}_3)\text{CH}_2\text{Ph}$. The considerable formation of these products indicates that these catalysts promoted the C-O bond cleavage through acidic actions to produce benzyl cation, which underwent two main reactions: stabilization by hydrogenation; attacking other species to cause rearrangement or condensation. Table 5 shows the results for dibenzyl (C-C linkage) at 400 - 425°C for 1 h with 9.8 MPa H_2 . The NiCl_2 - and MoCl_3 - LiCl-KCl catalysts showed essentially no effect at 400°C for breaking this type of C-C linkage. It is to be noted that the use of LiCl-KCl has neither positive nor negative effect on hydrogenation of polyaromatics such as anthracene, phenanthrene (Tables 1-2) and dibenzyl, but it showed pronounced effect in the runs of the ethers especially dibenzylether. For comparison of catalytic functions, we also conducted the model reactions using a commercial $\text{Ni-Mo/Al}_2\text{O}_3$ catalyst (Table 6), because it has high activity for hydrogenation of polyaromatics (20).

DISCUSSION

Catalytic Functions. In the earlier stage of this work, we inferred based on the high liquid yields in pyrolysis and in liquefaction of Wandoan coal that the NiCl_2 - and MoCl_3 - LiCl-KCl catalysts have higher hydrocracking ability (14). However, the model reactions using polyaromatics clearly showed that while they have hydrogenating ability, they do not possess high hydrocracking ability (Tables 1-2). In fact, their cracking ability is much lower than MoCl_3 or ZnCl_2 , and their hydrogenating ability is much lower than sulfided Ni-Mo commercial catalyst (20). The key question that arise is what are the key functions of the catalysts leading to high oil yields and coal conversions? The motivation of the later works on the pyrolysis, and model reactions presented in this paper comes from the desire to answer this question.

Analytical pyrolysis in N_2 is an useful technique for evaluating the coal reactivity and the effect of catalyst on the cleavage of bridge bonds. The pyrolysis showed that the NiCl_2 - and MoCl_3 - LiCl-KCl catalysts enhanced the formation of volatile materials from bituminous (Figure 2), subbituminous and brown coals in N_2 at the temperatures above 300°C (14,19). In fact, the yields of volatiles from non-catalytic pyrolysis up to 600°C can be obtained by the catalytic pyrolysis at 400°C (Figures 1-2). The fact that the temperatures for the appearance of catalytic enhancement in pyrolysis in N_2 correspond to the onset of H_2 uptake in the liquefaction of Akabira coal (Figures 2-3) and other coals indicates that the interactions between catalyst and coal and the participation of molecular H_2 begin to occur at the temperatures as low as about 300°C .

From the above results, it becomes clear that the NiCl_2 - and MoCl_3 - LiCl - KCl catalysts can promote the cleavage of connecting linkages in coal at low temperatures, followed by stabilization of the reactive fragments by transferable hydrogens in the internal (coal and its products) and external (H_2) hydrogen sources. The model reactions using the bridge-type compounds showed that they can promote the cleavage of C-O bond in ethers at low temperatures (Table 4). While the cleavage of C-C linkage in dibenzyl was not affected by the catalysts at 400°C (Table 5), there is a possibility that these catalysts can promote the C-C bond cleavage for the dinaphthylethane type C-C linkage, because the bond strength of the latter is lower than the former (210-235 vs. 255-258 KJ/mol, Table 3), and the latter is closer to that of bezylphenylether (221 KJ/mol, Table 3).

The liquefaction results showed that NiCl_2 - and MoCl_3 - LiCl - KCl significantly promote the production of oils without any significant increase in gas-make. The observed relationship between hydrogen consumptions and products distribution (Figures 4,6) suggests that the molecular H_2 was consumed mainly in producing oils in the catalytic runs. The results of model reactions in Tables 1-2 showed that adding LiCl - KCl to MoCl_3 and NiCl_2 suppressed extensive hydrocracking of polyaromatics, but retained their hydrogenation activity to produce partially hydrogenated species from 3- and 2-ring aromatics without remarkable ring-opening cracking. These results also confirmed the observation from ^1H NMR that the NiCl_2 - and MoCl_3 -based catalysts gave more hydroaromatic products in oils from both solvent-free (15,16) and tetralin-mediated coal liquefaction (Figure 7). The partially hydrogenated polyaromatics are also H-donors, which could be more effective than tetralin in terms of H-donation rate in coal liquefaction (17).

The cracking ability of the Lewis acid catalysts is determined mainly by their acid strength. When ZnCl_2 is used in coal liquefaction, it always increases the C1-C4 gas yield and the ratio of iso-C4 to n-C4, which has been taken as an acidity measure (2-3, 10). NiCl_2 - and MoCl_3 - LiCl - KCl do not remarkably enhance C1-C4 yields and the iso-C4/n-C4 ratio, because the ring-opening cracking and dealkylation were very limited. However, it is worthy while noting that *sym*-octahydrophenanthrene was also produced from anthracene in the catalytic runs (Table 1). Its yields increased with increasing MCln content, as shown in Figure 9. This is considered to be a result of acid-catalyzed isomerization of *sym*-octahydroanthracene. The extent of the isomerization shown in Figure 9 suggests that the acid strength of MCln - LiCl - KCl decreases with increasing LiCl - KCl content. We also observed some interesting trends in the case of ZnCl_2 . It was found that adding KCl to ZnCl_2 enhanced H-D exchange in H_2 -D2 model reactions, which is indicative of the enhanced ability for activating molecular H_2 upon KCl doping. On the other hand, ZnCl_2 - KCl afforded higher oil yield and coal conversion and lower gas yield with lower consumption of molecular H_2 , indicating the lower cracking ability and higher oil selectivity of ZnCl_2 - KCl relative to ZnCl_2 alone. This is a general trend in the solvent-free runs of many coals (9-11) including Wandoan coal (Figure 4).

The side reactions such as condensation (via benzyl cation) observed in model reactions (Table 4) seem to suggest that the hydrogenating ability of the NiCl_2 - and MoCl_3 -based catalysts is not sufficiently high. This trend is similar to that observed by Bell and co-workers for the reactions of ether compounds using ZnCl_2 (7-8), where the condensation reactions were more remarkable even at lower temperatures, 193 - 225°C . It should be noted that unsulfided and sulfided $\text{Ni-Mo/Al}_2\text{O}_3$ catalysts exhibited relatively similar activity in hydrogenating anthracene, phenanthrene (20) and dibenzyl, whereas the former also caused remarkable condensation in the reactions of the ethers (Table 6). On the other hand, the side reactions may be inhibited by H-donation during coal liquefaction. Apparently, the reactions of the bridge-type model compounds are far from the real situation, and the resulting data should not be over-emphasized.

The general implications from the above results are as follows: 1) To obtain high oil yields with catalysts, the extensive hydrocracking reactions such as those over MoCl_3 or ZnCl_2 are not necessarily required; such reactions will decrease oil yields and coal conversion and increase gas yields and H_2 consumptions; 2) It is critical to suppress the acidic cracking ability of the acid catalysts to achieve a better balance of hydrogenating ability with the cracking ability; 3) Selective reactions over dispersed catalysts, which begin to occur at low temperatures, can be more efficient in controlling coal depolymerization and promoting oil production. The target in primary liquefaction using multi-component catalysts is to obtain the products containing more oils and less asphaltene and preasphaltene with relatively lower H_2 consumption. The products should be derived under less-severe conditions and retain moderate reactivity for subsequent upgrading using supported catalysts.

Role of Catalyst Components and Retrogressive Reactions. The catalyst physical state and dispersion are also important factors, which have physical and/or chemical effect. Unlike ZnCl_2 or SnCl_2 which becomes molten salt at 313°C or 255°C , NiCl_2 and MoCl_3 do not melt even at 600°C . However, from DTA analysis of various salts (18), we found that they become molten when a mixture of 58%LiCl:42%KCl was added. The DTA suggested the melting points of the two catalysts to be 360°C and 387°C , respectively (14). The test using an electric furnace showed that at 400°C , $\text{NiCl}_2\text{-LiCl-KCl}$ is a homogeneous liquid, and $\text{MoCl}_3\text{-LiCl-KCl}$ exists in a semi-molten state. While the catalytic effects become measurable below their melting points (Figures 2-3), the molten state provides much better catalyst dispersion and more intimate contact with coal, which offers an advantage in controlling the depolymerization of solid coal. The addition of LiCl-KCl to NiCl_2 and MoCl_3 also causes the formation of some complex ions such as NiCl_4^{2-} and MoCl_6^{3-} at low and/or high temperatures (21). The decrease in the acid strength is probably associated with the formation of such complex ions. In addition, our preliminary tests showed that NiCl_2 can be reduced by H_2 at 400°C ; MoCl_3 is not readily reducible even by using K (molten potassium) but it disproportionates at the temperatures above $420\text{-}450^\circ\text{C}$. They appeared to become stable upon the addition of LiCl-KCl at the reaction temperatures.

Figure 10 shows a H-transfer network model modified from previous reports (16-17), and Figure 11 presents a general reaction model (22). Recent research has revealed that coal reactivity is higher than had been thought previously, and the liquefaction of coals under conventional process conditions involves considerable retrogressive reactions, as illustrated in Figure 11 (PRIOM formation), especially in the cases of subbituminous coals and lignites (22-24). The use of $\text{NiCl}_2\text{-}$ and $\text{MoCl}_3\text{-LiCl-KCl}$ has been found to be especially effective for liquefying subbituminous coals. While the relative effectiveness of these two catalysts changes with the coals used, it appears that they can significantly stabilize the coal-derived fragments by interaction, direct and indirect hydrogenation (Figure 10) to suppress their retrogressive reactions (Figure 11). Although the model reactions using ethers did not provide positive support, this consideration is strongly supported by the fact that very high oil yields (56-65%, daf) were obtained from the subbituminous coals by using these catalysts in the absence of any solvent (Figure 5), and the fairly high conversions (82-92%) are also an convincing evidence. In the runs of Akabira bituminous coals (16), the addition of tetralin was found to further increase coal conversions in the catalytic runs (84-86% to 91-94%), indicating that the use of H-donor solvent is also beneficial. However, such a effect in the catalytic runs was much smaller than in the non-catalytic runs (46 to 92%). It is likely that in the catalytic runs both H_2 gas and the hydroaromatic products (Figures 6-7) contributed to H-transfer (Figure 10), in addition to the H-donation from solvent and from coal itself. In the non-catalytic runs at 400°C (16,22), the effect of tetralin addition appeared to be smaller for converting subbituminous coals such as Wandoan coal (49 to 61%) than for bituminous coals. It is to be noted that McMillen, Malhotra and co-workers (27-28) proposed that hydroaromatics can induce the cleavage of some strong bonds through radical hydrogen transfer.

CONCLUSIONS

The liquefaction of five coals established the general effectiveness of the two new ternary catalysts, $\text{NiCl}_2\text{-}$ and $\text{MoCl}_3\text{-LiCl-KCl}$ both in solvent-free runs and in the runs with added tetralin. The catalysts begin to interact with coal and exert measurable effects on coal pyrolysis in N_2 and the participation of molecular H_2 in coal liquefaction at the temperatures as low as about 300°C . The desirable features of these catalysts in coal liquefaction are characterized by the high oil yields and high conversions, and that molecular H_2 is mainly consumed in producing oils without remarkable increase in gas-make. The active components in the ternary catalysts are NiCl_2 and MoCl_3 , in which the LiCl-KCl acts to adjust (decrease) the acidity and to suppress the cracking ability, which contributes to balancing the catalytic functions. At the temperature of 400°C , NiCl_2 and MoCl_3 are solubilized and stabilized by LiCl-KCl , producing a chemically more stable, but mobile catalyst phase which is important for controlling coal depolymerization. LiCl-KCl binary salts are inactive for pure hydrocarbons but can interact with some heteroatom-containing structures such as ethers. In the presence of tetralin solvent, $\text{NiCl}_2\text{-}$ and $\text{MoCl}_3\text{-LiCl-KCl}$ increase the gas-phase H_2 consumption but decrease the net hydrogen transfer from tetralin; the use of LiCl-KCl remarkably reduces the H_2 consumption without any negative impact on product yields. The $\text{NiCl}_2\text{-}$ and $\text{MoCl}_3\text{-}$ based catalysts play a key role in promoting oil production from the coals, increasing the contents of hydroaromatics and decreasing O and N contents of oils, probably by enhancing the cleavage of some connecting linkages and selectively promoting the hydrogenation of polyaromatics (to create in-situ H-donors).










FUTURE RESEARCH

The present research contributes to an improved understanding of the key factors for developing novel multi-component, dual-functional catalysts. The catalysts examined and the conditions used, however, are not considered to be the best. Temperature-programmed pyrolysis and t-p profiles for liquefaction of coals suggest that coals can be liquefied at the temperatures below 400°C. The future work on the acid catalysts should be directed toward the low-severity liquefaction. Efforts should be made to minimize the catalyst loading, and achieve better balance of catalytic functions (suppressing the acid strength and/or increasing hydrogenating ability) by exploring novel formulations. For the effects of various catalysts, more attention should be given to liquefying low-rank coals, and to increasing oil yields (rather than the conversions to THF solubles). The coal pretreatment followed by low-severity liquefaction using novel acidic dispersed catalyst should be tested in the future work. An interesting two-stage coal depolymerization procedure involving the use of Lewis acid such as FeCl₃ (3-20 wt% on coal) in the first stage and a base in the second stage at the temperatures of 250-310°C has been proposed by Shabatai and co-workers (27-28). Their results and our results suggest that selective reactions of coals at low temperatures in the presence of specific acid catalysts can be very effective in promoting coal depolymerization and oil production. If more effective dispersed catalysts for primary liquefaction and the supported catalysts with proper pore structure (29) for upgrading coal liquids, can be developed and applied, further reduction in severity of the current two-stage liquefaction processes (400-460°C, 17-20 MPa) is practically possible.

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
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Table 1. Hydrogenation and Cracking of Anthracene

Run No.	1	2	3 ^a	4 ^b	5	6
Catalyst	None	LiCl-KCl	MoCl ₅ -LiCl-KCl	NiCl ₂ -LiCl-KCl	MoCl ₅	NiCl ₂
Products ^c (wt%)						
C ₁ -C ₄	0.1	0.2	0.9	0.2	2.6	0.2
C ₅ -C ₉	-	-	0.1	-	2.1	0.7
R ₁ -R ₂	-	-	0.9	-	1.1	-
R ₁ -R ₂ + 	0.1	0.1	3.0	0.8	40.2	1.6
R ₁ -R ₂ + R ₂	0.2	0.1	0.6	0.1	1.8	0.1
 + 	0.3	0.1	7.7	4.3	15.6	11.4
 + 	-	-	10.4	8.0	9.7	15.8
	14.9	15.8	44.9	41.0	6.4	37.3
	69.3	66.4	19.9	30.2	-	21.0
	14.4	13.8	6.4	12.1	2.4	7.6
	-	-	2.1	1.6	8.7	4.0
Conversion	85.6	86.2	93.6	87.9	97.6	92.4

a-b) Molar contents of MoCl₅ (a) and NiCl₂ (b) are 12% and 14%, respectively; c) R₁ and R₂ mean alkyl groups or hydrogen; d) ungu-Octahydroanthracene; e) 4,9m-Octahydroanthracene; f) 4,9m-Octahydroanthracene

Table 2. Hydrogenation and Cracking of Phenanthrene

Run No.	9	10	11	12	13	14
Catalyst	None	LiCl-KCl	MoCl ₅ -LiCl-KCl	NiCl ₂ -LiCl-KCl	MoCl ₅	NiCl ₂
Products ^a (wt%)						
C ₁ -C ₄	-	0.1	0.1	0.2	3.4	0.1
C ₅ -C ₉	0.2	-	-	0.1	10.4	0.3
R ₁ -R ₂	0.1	-	0.5	-	10.1	0.1
R ₁ -R ₂ + 	0.4	-	-	0.1	27.1	0.2
R ₁ -R ₂ + R ₂	-	-	-	-	1.1	0.1
 + 	-	-	0.1	0.1	10.2	0.9
 + 	-	-	-	0.8	5.3	1.6
	0.7	1.0	0.3	-	2.1	0.1
	0.8	0.9	1.5	6.0	4.6	9.7
	1.3	1.4	6.3	8.2	9.7	12.0
	96.3	95.4	90.9	83.4	13.9	74.1
Conversion	3.7	4.6	9.1	16.6	86.1	25.9

a) R₁ and R₂ mean alkyl groups or hydrogen; b) including cyclohexyl phenyl ethane; c) ungu- and d) 4,9m-Octahydrophenanthrene.

Table 3. Dissociation Energy of C-O and C-C Bonds (Fl. Energy, exp. rep.)

Structure	BDI, kcal/mol	Ref.	Structure	BDI, kcal/mol	Ref.
O-C linkage	221	a	O-C linkage	258, 255	b, c
Ph-O-CH ₃	318	b	PhO ⁺ -CH ₃ ⁺	235	e
PhO-PhH	327+8	b	PhO ⁺ -CH ₂ -Ph ⁺	210	f
PhO-PhH	331	b	PhO ⁺ -CH ₂ -Ph ⁺	288	d
CH ₃ -CO-CH ₃	331	c	PhO ⁺ -CH ₂ -CH ₂ -Ph ⁺	343	d
CH ₃ -CO-CH ₃	335	c	PhO ⁺ -CH ₂ -CH ₂ -Ph ⁺	349	f
			CH ₃ -CO-CH ₃	380(13)	g
C-C bond	251	d	PhO ⁺ -CH ₂ -Ph ⁺	325(13), 350,	b, f
ac ⁺ -CH ₂	285	d	PhO ⁺ -CH ₂ -Ph ⁺	486, 480, 419	d, f, c
PhO ⁺ -CH ₂	301, 364	d, f	Ph ⁺ -Ph		

Benzylphenylether	Dibenzylether
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Reactant	Catalyst	Products (wt%)	Benzene			MCH			None			None			None		
			LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl	LICI-NCl
			0.1	0.3	1.3	7.6	-	-	0.3	0.2	0.3	-	-	-	-	-	
			25.2	19.9	3.8	5.8	-	-	65.6	34.3	23.2	25.3	-	-	-	-	
			42.3	33.7	30.2	43.8	-	-	-	-	-	-	-	-	-	-	
			-	-	1.0	6.2	-	-	6.8	5.3	-	-	-	-	-	-	
			-	-	-	-	-	-	6.2	16.8	-	-	-	-	-	-	
			2.9	1.1	-	-	-	-	6.1	45.3	-	-	-	-	-	-	
			1.0	8.4	3.5	-	-	-	-	-	-	-	-	-	-	-	
			15.0	14.2	39.8	21.3	-	-	8.8	2.1	tr.	12.3	-	-	-	-	
			4.2	1.6	tr.	1.0	-	-	0.8	0.7	11.6	7.6	-	-	-	-	
			3.0	3.2	13.7	3.3	-	-	2.5	0.2	25.8	20.1	-	-	-	-	
			97.1	96.9	100.0	100.0	-	-	93.9	54.7	100.0	100.0	-	-	-	-	

coll: (none)

Table 5. Reaction of Diphenyl at 400-425°C for 1 hr.

Temperature	400°C				425°C			
	None	LiCl-NiCl ₂	LiCl-NiCl ₂ -MoCl ₅ ³	None	LiCl-NiCl ₂	LiCl-NiCl ₂ -MoCl ₅ ³	None	LiCl-NiCl ₂ -MoCl ₅ ³
Catalyst	None	LiCl-NiCl ₂	LiCl-NiCl ₂ -MoCl ₅ ³	None	LiCl-NiCl ₂	LiCl-NiCl ₂ -MoCl ₅ ³	None	LiCl-NiCl ₂ -MoCl ₅ ³
Product (wt%)	0.2	0.3	0.4	1.5	2.5	1.9	3.2	3.3
Benzene	0.8	1.4	1.1	1.3	5.7	6.2	8.3	8.7
Toluene	0.8	1.4	1.1	1.3	5.7	6.2	8.3	8.7
Diisobutylene	97.9	97.3	96.2	95.5	83.6	86.6	76.0	76.0
Diisobutyl	97.9	97.3	96.2	95.5	83.6	86.6	76.0	76.0
Conv. (M%)	2.1	2.7	3.8	4.3	18.6	16.7	21.5	20.4

[illegible][illegible]

a) Runs at 400°C for 1 h with 9.8 MPa H₂; b) Runs at 350°C for 1 h with 4.9 MPa H₂; c) Commercial (KF-153S) sulfided (S-NiMo) and unsulfided (Ni-Mo) catalysts; d) Runs at 350°C for 1 h with 4.9 MPa H₂; e) Runs at 350°C for 1 h with 4.9 MPa H₂; f) Runs at 350°C for 1 h with 4.9 MPa H₂; g) Runs at 350°C for 1 h with 4.9 MPa H₂; h) Runs at 350°C for 1 h with 4.9 MPa H₂; i) Runs at 350°C for 1 h with 4.9 MPa H₂; j) Runs at 350°C for 1 h with 4.9 MPa H₂; k) Runs at 350°C for 1 h with 4.9 MPa H₂; l) Runs at 350°C for 1 h with 4.9 MPa H₂; m) Runs at 350°C for 1 h with 4.9 MPa H₂; n) Runs at 350°C for 1 h with 4.9 MPa H₂; o) Runs at 350°C for 1 h with 4.9 MPa H₂; p) Runs at 350°C for 1 h with 4.9 MPa H₂; q) Runs at 350°C for 1 h with 4.9 MPa H₂; r) Runs at 350°C for 1 h with 4.9 MPa H₂; s) Runs at 350°C for 1 h with 4.9 MPa H₂; t) Runs at 350°C for 1 h with 4.9 MPa H₂; u) Runs at 350°C for 1 h with 4.9 MPa H₂; v) Runs at 350°C for 1 h with 4.9 MPa H₂; w) Runs at 350°C for 1 h with 4.9 MPa H₂; x) Runs at 350°C for 1 h with 4.9 MPa H₂; y) Runs at 350°C for 1 h with 4.9 MPa H₂; z) Runs at 350°C for 1 h with 4.9 MPa H₂.

Ph: Phenyl; e) Including ethyl and dimethylbenzenes.

a) $\text{C}_2\text{H}_5\text{NO}_2$ and $\text{C}_2\text{H}_5\text{NO}$

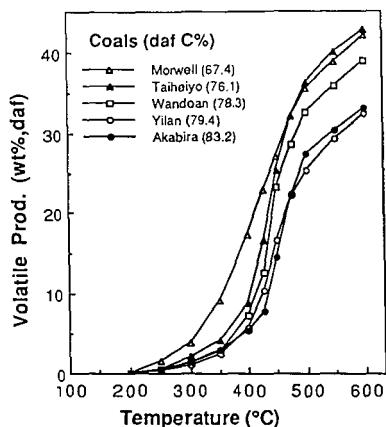


Figure 1. Coal pyrolysis in N₂ up to 600°C.

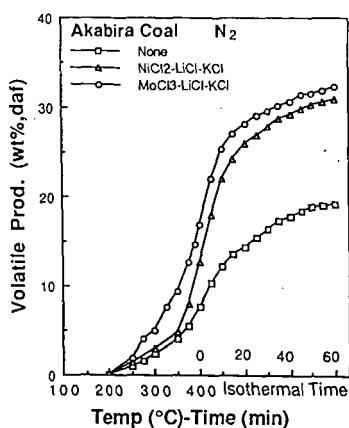


Figure 2. Pyrolysis of Akabira coal in N₂.

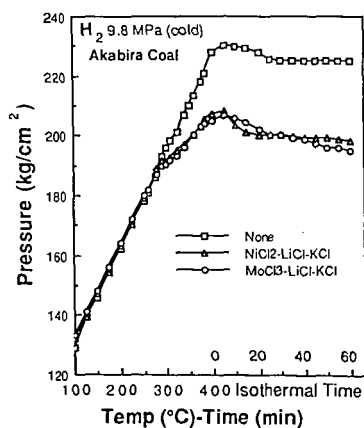


Figure 3. Reactor t-p profiles for liquefaction.

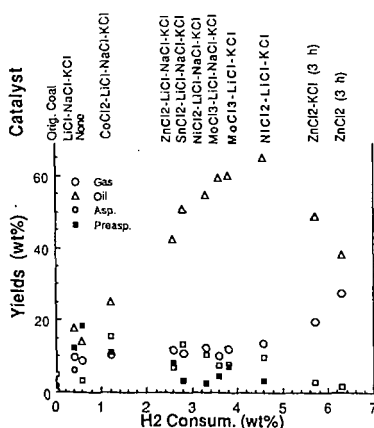


Figure 4. Dry liquefaction of Wandoan coal.

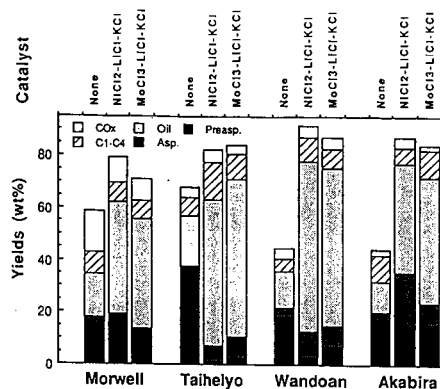


Figure 5. Dry liquefaction of coals.

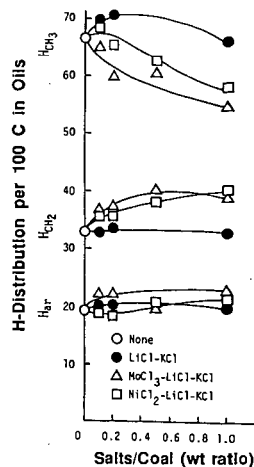


Figure 7. H-distribution of oils

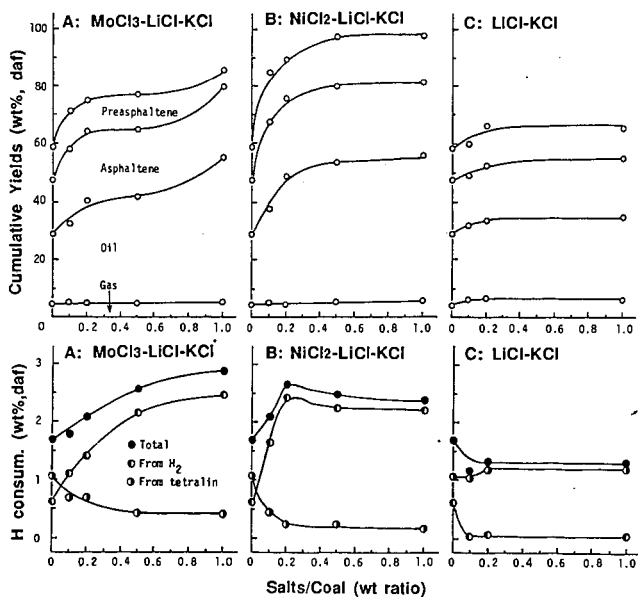


Figure 6. Effect of salt loading on coal conversion and H-transfer under low H_2 pressure

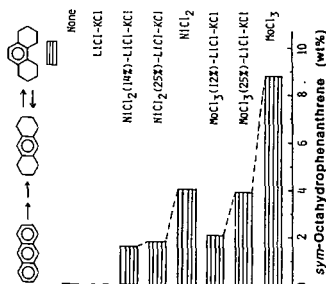


Figure 9. *sym*-octahydrophenanthrene from anthracene

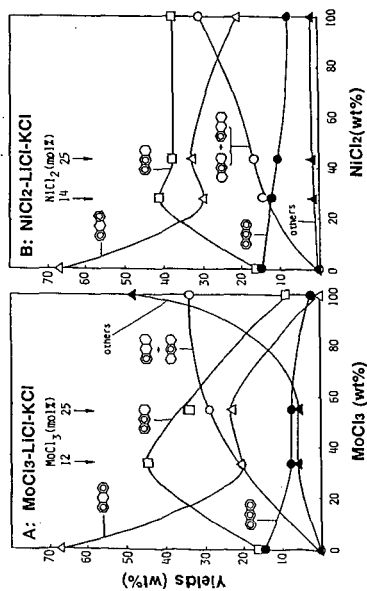


Figure 8. Effect of MCIn content on hydrogenation of anthracene

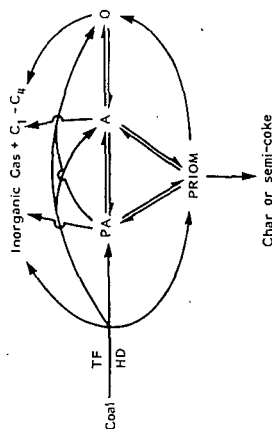


Figure 11. A reaction model for coal liquefaction

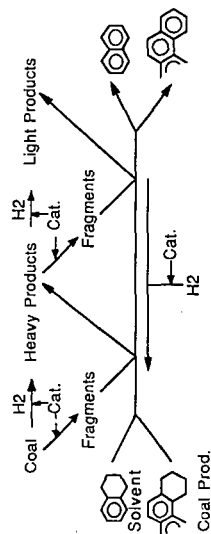


Figure 10. Hydrogen-transfer network in liquefaction